STABLE VINYL ALCOHOLS

BY

CARLETON ANGELO SPERATI

B.A., Luther College, 1938
M.A., University of Illinois, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

The problem of enol-keto tautomerism has long intrigued organic chemists. Since 1880, when Erlenmeyer[1] formulated his rule that no hydroxyl group could exist on a carbon atom containing a double bond, a large number of enols have been prepared and studied. However, chelation is possible in almost all of these. In enols from α-diketones the enol group is part of a hetero-conjugated system.

Kohler[2] isolated an enol, 1,2,3,3-tetraphenyl-1-propen-1-ol, but it was very unstable and he did not characterize it. However, he made an enol peroxide from this as well as other unstable enols. The fact that an enol from benzhydrylacetomesitylene was very persistent in solution was shown by Kohler, Tishler, and Potter.[3] In spite of its comparative stability the pure stable enol could not be isolated.

The discovery[4] that 1,2-dimesityl-1-propen-1-ol (I) could be isolated furnished the first example of a truly stable vinyl alcohol containing, besides the enol group, only hydrocarbon residues. This material is very similar, in many respects, to the compound prepared by Lutz and Kibler.[5]

$$\begin{array}{l} \quad\quad CH_3\ \ OH \\ \quad\quad\ \ |\quad\ \ | \\ *\ MesC = CMes \end{array} \qquad \text{I}$$

The structure of I was shown by formation of an acetate, and evidence from infra-red absorption spectra.[4] Confirmatory evidence has been presented by Fuson, Byers, Rabjohn and Armstrong.[6] They found that I can be ketonized by the action of methanolic hydrogen chloride, and the keto form enolized by sodium ethylate. Ozonization cleaved the enol or its acetate, forming acetomesitylene and mesitoic acid. These same pro-

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* Mes and Dur are mesityl and duryl, respectively.

ducts were formed by passing oxygen through a solution of the enol or by oxidative cleavage in air over a period of about six weeks. In contrast to this action, permanganate dehydrogenated the enol to form ∝-mesitylvinyl mesityl ketone from which the enol had been prepared by catalytic hydrogenation.

The research reported here was concerned with the study of the preparation and properties of some analogues of I.

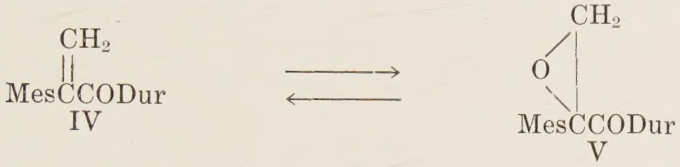
Discussion and Experimental

A stable vinyl alcohol, 1-duryl-2-mesityl-1-propen-1-ol (II), was prepared by a scheme of reactions similar to that used in the preparation of I.[4] Although it does not revert spontaneously to the keto form (III), it may be ketonized by the action of methanolic hydrogen chloride. Also like I the keto form may be enolized with sodium ethylate. Neither the Grignard reagent nor acetic anhydride had any effect on the ketonic modification.

II was more stable to air oxidation than was I, but 1-isoduryl-2-mesityl-1-propen-1-ol, on the other hand, was readily attacked. In one experiment a small amount of a white solid, whose composition indicated the presence of three oxygen atoms in the molecule, was isolated. This was very likely the enol peroxide, and indicates that the decomposition in air involves this unstable intermediate. Three other similar enols were prepared. They are 1-(2,4,6-triethylphenyl)-2-mesityl-1-propen-1-ol, 1-mesityl-2-isoduryl-1-propen-1-ol and 1-mesityl-2-duryl-1-propen-1-ol. The action of permanganate on each of these stable vinyl alcohols regenerated the ∝-arylvinyl aryl′ ketone from which it was prepared. For example, enol II was prepared from and may be converted into ∝-mesitylvinyl duryl ketone (IV).

Additional evidence for the structure of the ∝-arylvinyl

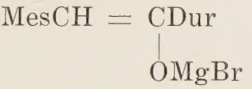
aryl' ketones was obtained when it was found that ∝-mesitylvinyl duryl ketone (IV) formed an oxido derivative (V) through the action of alkaline hydrogen peroxide on this ∝,β-unsaturated ketone.



The action of methylmagnesium iodide on the epoxide regenerated the vinyl ketone. These results were confirmed by the preparation of oxido ∝-mesitylvinyl 2,4,6-triethylphenyl ketone and oxido ∝-mesitylvinyl isoduryl ketone. Treatment of this last compound with methylmagnesium iodide regenerated ∝-mesitylvinyl isoduryl ketone.

In connection with the synthetic work in making the stable vinyl alcohols, we desired an improved procedure for the preparation of arylacetic acids. A possible route was the oxidation of β-arylethyl alcohols such as mesitylethyl alcohol. The oxidation did not prove satisfactory, but a method of preparation of mesitylethyl alcohol, far superior to that of Sordes,[7] was developed. It consists of the reaction of mesitylene with ethylene oxide in the presence of aluminum chloride. 2,4,6-Triethylphenethyl alcohol was also made by this procedure.

It seemed likely that the methyl group on the double bond in the vinyl alcohol was not necessary for stability. Therefore some reactions of the enolate of 2,4,6-trimethylbenzyl duryl ketone (VI) were studied.



The enolate was prepared by the action of ethylmagnesium bromide on the ketone. Decomposition of the enolate regenerated the original ketone. The enolate formed a mono bromo derivative by the addition of bromine, and a

benzoyl derivative by reaction with benzoyl chloride. An enol benzoate structure is postulated for the benzoyl derivative as it was hydrolyzed to give the desoxybenzoin under conditions that Kohler, Tishler and Potter[3] found did not cleave similiarly substituted β-diketones. The conclusion that can be drawn from these data is that at least one form (cis-trans) of the hindered desoxybenzoin is not stable in the enol form.

Summary

Five new stable vinyl alcohols were prepared and some of their properties were studied.

In contrast to the results Kohler, Richtmyer and Hester[8] obtained in a study of the action of the Grignard reagent on unhindered α-oxido ketones, two hindered derivatives reacted with methylmagnesium iodide to regenerate the original unsaturated ketone.

An enol benzoate was obtained from the reaction between benzoyl chloride and the bromomagnesium enolate of 2,4,6-trimethylbenzyl duryl ketone.

In connection with the preparation of these vinyl alcohols and derivatives a number of new substituted benzyl chlorides, arylacetonitriles, arylacetic acids and mixed, hindered desoxybenzoins were made. An improved procedure for the preparation of mesitylethyl alcohol was also developed.

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VITA

The writer was born in Fergus Falls, Minnesota, on September 1, 1918. He received his elementary education in the Model School of Park Region College in Fergus Falls, and in the public schools of that city. He was graduated from Washington High School in Fergus Falls in May, 1934. He attended Luther College, Decorah, Iowa, from 1934 to 1938 and was granted a Bachelor of Arts degree from that institution in June, 1938. In the fall of that year he entered the Graduate School of the University of Illinois and received the Master of Arts degree in 1939. He was the receipient of a University scholarship for the year 1938-1939, and held University fellowships during the years 1939-1940 and 1940-1941.

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